

Polarization fields in nitride nanostructures: theory and practical implications

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Huge built-in electric fields are predicted to exist in wurtzite III-V nitrides thin films and multilayers. Such fields originate from heterointerface discontinuities of the macroscopic bulk polarization of the nitrides. We discuss the theoretical background and the intriguing practical implications of polarization fields for nitride nanostructures.

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III-V nitrides represent a new frontier of semiconductor physics. One of their unusual basic properties, macroscopic polarization, offers unique opportunities for device design and basic investigations. Polarization manifests itself as built-in electrostatic fields in polarized materials interfaced to different media. These fields affect the characteristics, performance, and response of multilayer nanostructured devices. In this Letter we discuss the theoretical basis and practical implications of polarization fields in nitride nanostructures. Polarization fields turn out to give III-V nitrides a considerable potential for novel device design and simulations.

General – The dipole moment per unit volume of a finite dielectric is the *longitudinal* polarization \mathbf{P}_L , also identified with (minus) the screened field generated by the net polarization charge at the sample surfaces. \mathbf{P}_L is experimentally accessible, but its direct calculation is impractical. Recent advances [1,2] have provided a route to this quantity through a novel, rigorous definition of the polarization in a periodic system: the *transverse* polarization \mathbf{P}_T is the gauge-invariant Berry's phase of the Bloch orbitals, accumulated in an adiabatic transformation of the system from some reference state to its actual state [1]. \mathbf{P}_T , which can equivalently be viewed as the integrated polarization current flowing through the crystal during the transformation, has no relation with the charge density of the polarized dielectric. Importantly, \mathbf{P}_T can now be calculated accurately from first-principles density-functional calculations [1,3–5]. A key point is that the *absolute* polarization of a material can be obtained with no arbitrariness by referencing its polarization to that of a system for which $\mathbf{P}=0$ by symmetry or otherwise. For wurtzite nitrides [4], this may be vacuum or the zincblende phase. Finally, although not directly measurable, \mathbf{P}_T gives access to \mathbf{P}_L through the classical relation

$$\mathbf{P}_T = \vec{\epsilon}_0 \mathbf{P}_L, \quad (1)$$

once the static dielectric tensor $\vec{\epsilon}_0$ has been measured or computed [5]. Here we deal with the total polarization (either longitudinal or transverse) $\mathbf{P} = \mathbf{P}^{(0)} + \delta\mathbf{P}(\epsilon)$ in a given strain state at zero temperature, in the absence of external fields. We point out that in wurtzite nitrides the

total polarization at zero strain, known as spontaneous, is non-zero and large. Unlike the strain-induced piezoelectric terms $\delta\mathbf{P}(\epsilon)$, the spontaneous polarization has a fixed direction and magnitude for any crystal structure.

The polarization of a material A manifests itself when its bulk periodicity is broken, e.g. as a local charge accumulation at the interface with a different medium B . Therewith only polarization differences are accessed, as required by theory. If the interface is insulating and gap-states-free, it can be proven [2] that the areal interface charge density is

$$\sigma_{\text{int}} = \pm \hat{\mathbf{n}} \cdot (\mathbf{P}_L^A - \mathbf{P}_L^B), \quad (2)$$

where $\hat{\mathbf{n}}$ is the interface normal, and the sign of σ_{int} depends on the relative orientation of the media. This equality has been verified directly in ab initio calculation on nitride interfaces [5,6]; the polarization charge density was found to be typically $\sim 5 \times 10^{12} \text{ cm}^{-2}$, localized in an interface region less than $\sim 5 \text{ \AA}$ thick. As a consequence of this charge accumulation [7], macroscopic electrostatic fields (screened by electronic and ionic responses) exist in the interfaced media. For the moment, we assume that these fields are uniform. Due to Gauss' law, upon crossing the interface the field changes by

$$\Delta\mathbf{E} = 4\pi\hat{\mathbf{n}}\sigma_{\text{int}}. \quad (3)$$

In the absence of external fields, the values of the fields in the interfaced media are determined by the bulk polarizations of the layers involved in the structure. For example, the electrostatic field in a finite, isolated, and surface-state free slab of a polarized material is $-4\pi \mathbf{P}_L$. The field in the vacuum is zero by construction because of the overall neutrality of the slab. Similarly, if two slabs of differently polarized materials A and B are interfaced to form a finite and isolated A/B slab the fields will equal $-4\pi \mathbf{P}_L^A$ in material A and $-4\pi \mathbf{P}_L^B$ in material B , and the field in the vacuum will again be zero. It is straightforward to show that this follows directly from the superposition principle of electrostatics.

We now discuss the role of polarization fields in structures (overlayers, quantum wells, superlattices) of relevance to device applications of III-N compounds and alloys, starting with the issue of free-carrier screening.

Screening – Uniform electrostatic fields, such as those generated by macroscopic polarization discontinuities, may not be sustained by an arbitrarily thick sample [8]. At *zero temperature* the field-induced potential drop across the system will be larger than the band gap for thickness $l \geq l_c \sim E_{\text{gap}}/|\mathbf{E}| = E_{\text{gap}}/4\pi\sigma$. The metastable state thus realized, whereby the valence edge at one end of the sample is higher than the conduction edge at the other end, can reach the ground state by charge tunneling across the sample, typically in very long times.

By contrast (e.g.) *at room temperature*, the presence of free carriers forbids the existence of a non-zero *uniform* macroscopic field, as the latter would cause a permanent current to flow across the sample in the absence of an external electromotive power. The paradox is resolved by the very presence of free carriers, which screen the field away from the interface. In the small-field Thomas-Fermi picture, the field decays exponentially with characteristic lengths of order $0.1 \mu\text{m}$ for the nitrides. This is of course irrelevant for nanostructure layers of $\sim 50 \text{ \AA}$ in size. However, the fields involved in typical nitride structures are of order 100 MV/m (see below), so that the small-field limit is invalid, and the full description of (classical) space charge layers must be applied [9]: the field is then screened out over typical lengths as small as 10 \AA [10]. This strong screening would prevent the field-induced potential drop to exceed significantly $k_B T$ [9]. However, one should be aware that the fields in question are also large enough to require a quantum treatment of the space charge distribution; since typical wavefunctions extend over $\sim 60 \text{ \AA}$ [10], the over-exponential [9] damping of the field may be preempted in sufficiently thin layers. While quantitative predictions require a full quantum treatment for general fields and the specifics of device parameters, it is sensible to expect essentially uniform fields up to layer thicknesses of order $100\text{-}150 \text{ \AA}$ in the nitrides. In any case, it must be kept in mind that the polarization field contributions to the nanostructure potential are *fixed* elements of that potential, that may be screened to different extents by free carriers or otherwise, depending on the specific application, geometry, and material.

Carrier screening also preempts dielectric breakdown in massive samples. This might be a serious possibility, since the uniform fields in the absence of free carriers ($\sim 500 \text{ MV/m}$) are much larger than the dielectric breakdown fields of high power dielectrics ($10\text{-}50 \text{ MV/m}$). Of course, breakdown is not an issue in thin nanostructures.

Overlayers – We now consider a polarized pseudomorphic overlayer on a thick heterogeneous substrate, assuming the system to be insulating and surface/interface-states-free. The layer surface and its interface to the substrate are charged, and a surface-normal electrostatic field exists inside the overlayer. In the absence of external fields, the internal field is

$$\mathbf{E} = 4\pi\hat{\mathbf{n}}\sigma^{\text{surf}} = -4\pi(\hat{\mathbf{n}} \cdot \mathbf{P}_L^{\text{overl}})\hat{\mathbf{n}} \quad (4)$$

with $\hat{\mathbf{n}}$ the surface normal versor. To simplify notation, we henceforth restrict ourselves to (0001)-grown nitride layers where the total bulk polarization \mathbf{P}_L is surface-normal, hence $(\hat{\mathbf{n}} \cdot \mathbf{P}_L^{\text{overl}})\hat{\mathbf{n}} = \mathbf{P}_L$.

The result Eq. (4) stems again from the superposition principle. In this configuration, there is a direct proportionality between longitudinal polarization and electrostatic field in the layer. In particular, if the overlayer is unstrained, the field is proportional to the spontaneous polarization. The latter has been calculated [4] to be negative for all the III-V nitrides, so that \mathbf{E} will point in the (0001) direction. According to Eq. (4), typical values for the electrostatic fields in unstrained overlayers range from 250 MV/m (InN) to 900 MV/m (AlN) (at least in the regime where screening is not yet playing a role). Typical polarization charge densities at the relevant interfaces are in the 10^{12} cm^{-2} . Overlayers strained in the a -plane carry in addition a piezoelectric polarization along the c axis. Due to the huge piezoelectric constants of III-V nitrides [4], the piezoelectric and spontaneous polarizations are generally comparable in magnitude. Epitaxial strains, depending on their sign and size, may then cause a strong increase and/or a sign reversal of the total polarization.

As an example of the practical consequences of the above, consider the band offset at an A/B heterojunction, experimentally determined via XPS core level alignment as

$$\Delta E_v = [E_{cl}^A - E_v^A]^{\text{bulk}} - [E_{cl}^B - E_v^B]^{\text{bulk}} + \Delta E_{cl}^{\text{int}}, \quad (5)$$

with $\Delta E_{cl}^{\text{int}}$ the core level binding energy difference measured at the interface. Since XPS is surface sensitive, this definition is only meaningful if $\Delta E_{cl}^{\text{int}}$ is independent of the overlayer thickness. In a polarized overlayer, the internal electric field will shift the core binding energies linearly with the atom's distance from the interface; the XPS signal will shift accordingly, as its leading term originates from the topmost layers. Because of this shift, the band offset has to be extracted by linear extrapolation to null layer thickness of a series of measured $\Delta E_{cl}^{\text{int}}$. The ratio shift/thickness, in turn, gives directly the screened polarization field (Eq.(4)).

A recent investigation [11] of band offsets at the strained 2H-AlN/6H-SiC(0001) interface has indeed revealed this effect. The extrapolated value of the band offset agrees with ab-initio predictions [12]. Using the theoretical polarization values [4], we predict a linear shift of the core levels in the (0001)-oriented [11] overlayer of 55 meV/\AA , whereby the spontaneous and piezoelectric contributions are about 80 meV/\AA and -25 meV/\AA respectively. The experimental shift [11] has the same sign, and a somewhat smaller magnitude ($\sim 30 \text{ meV/\AA}$); this deviation from the predicted value may be due to the

presence of surface states at AlN (0001) [13], which pin the Fermi level affecting the field-induced shift (i.e., surface states partly compensate the effect of the $\sim 10^{12}$ cm $^{-2}$ polarization charge density, though of course not the charge itself). It is important to note that the neglect of the spontaneous polarization would lead to a shift *opposite* in sign to that observed.

Finally, it is worth mentioning that the picture does not change for polarized overlayers on *polarized* substrates. Indeed, as seen from the overlayer and the vacuum, the substrate is neutral overall, and produces no uniform field.

Quantum wells – While in polarized overlayers the field is proportional to the overlayer’s \mathbf{P}_L , it is easy to prove using the superposition principle of electrostatics that in an isolated, symmetric (A-B-A) quantum well (QW) the field generated by interface charge accumulation at the well’s borders is proportional to the polarization difference $\Delta\mathbf{P}_L$ between cladding and active layers,

$$\mathbf{E}_{\text{QW}} = 4\pi\hat{\mathbf{n}}\sigma^{\text{int}} = -4\pi\Delta\mathbf{P}_L, \quad (6)$$

while the field outside the QW is exactly zero. Within the QW, the field is effectively uniform, since typical screening lengths are larger than typical well thicknesses. The assumption of isolated well implies that the cladding layers are sufficiently thick in order that influences from their interface to the outer world get screened out; if this were not the case, free-carriers-screened field contributions from the far interfaces would affect the field in the QW. As a consequence of Eq. (6), if the composition of the cladding layers differs mildly from that of the well, the internal QW field may much be smaller than the absolute polarization value in the material itself. By the same token, the QW may be made of an *unpolarized* material and yet have a non-zero internal field, since the latter is controlled only by the polarization *difference* with the outer world.

The main effect of internal fields in QWs is to separate spatially photogenerated or injected carriers of opposite sign. As a consequence, an increase in well thickness will cause increased recombination times, reduced interband transition matrix elements, and red-shifted interband transitions. These effects have been studied in biased unpolarized QWs [14], and an application to polarized nitrides appeared recently [15]. Note that, since the field is zero outside the well, the bound states are not metastable, and no phenomenon due to finite escape times is expected as in classic biased QWs.

An important point about the red shift in QWs is its reversibility. In random/ordered/random GaInP $_2$ alloy QWs [16], where built-in polarization fields have been observed, one finds that applying an appropriate external field the transition energy increases, saturating at the value corresponding to flat-bands conditions in the active layer: the external bias effectively “rectifies” the polar-

ized well potential. Of course, this effect can be used to measure the field, hence the polarization, inside the QW.

Superlattices – In superlattices, the field-polarization relation can become highly complex. In general, there are no null-field regions, and no simple proportionality between field and polarization. The electrostatic field in a superlattice has the same period of the superlattice itself, so that the average electrostatic field $\langle E \rangle$ is null, i.e. there is no uniform field throughout the whole system. For typical layer thicknesses, within each homogeneous layer, the field is uniform, and at each interface one has

$$\Delta\mathbf{E} = -4\pi\Delta\mathbf{P}_L. \quad (7)$$

In the case of alternating layers of materials A and B , of dielectric constants ε_A and ε_B and respective thicknesses l_A and l_B , using Eqs. (2)-(3) and periodic boundary conditions, the field in A is easily seen to be

$$\mathbf{E}_A = -4\pi l_B(\mathbf{P}_T^A - \mathbf{P}_T^B)/(l_A\varepsilon_B + l_B\varepsilon_A), \quad (8)$$

and analogously for B . If the two layers have the same thickness, [5]

$$\mathbf{E}_A = -4\pi(\mathbf{P}_T^A - \mathbf{P}_T^B)/(\varepsilon_A + \varepsilon_B), \quad (9)$$

and similarly for B . The presence of these fields, besides its possible practical consequences, offers yet another way to measure the absolute spontaneous polarization of a given material. If one of the layers (say, B) is made of unpolarized material, such as GaN in the zincblende structure, Eq. (9) becomes

$$\mathbf{E}_A = -4\pi\mathbf{P}_T^A/(\varepsilon_A + \varepsilon_B) \quad (10)$$

whence \mathbf{P}_T^A is extracted.

Solid solutions – Solid solutions are ubiquitous in heterostructure applications. Their polarization is an important parameter for simulations, and to a first approximation it can be predicted by linear interpolation of the polarizations of bulk III-nitrides [4]. Assuming that the relevant piezoelectric tensors \vec{e} [4] and strain field $\vec{\epsilon}$ are known, the transverse polarization of a pseudomorphically strained, e.g., InGa N solid solution is

$$\begin{aligned} \mathbf{P}_T(\text{In}_x\text{Ga}_{1-x}\text{N}) \simeq & x\mathbf{P}_{\text{InN}}^{(0)} + (1-x)\mathbf{P}_{\text{GaN}}^{(0)} \\ & + [x\vec{e}_{\text{InN}} + (1-x)\vec{e}_{\text{GaN}}]\vec{\epsilon}(x), \end{aligned} \quad (11)$$

containing terms linear as well as quadratic in x (similar relations hold for quaternary solutions). The third term on the rhs of Eq. (11) is only present in pseudomorphic strained growth, and will tend to zero beyond the critical thickness at which strain relaxation sets in.

This Vegard-like approach will only yield a rough estimate: it is established [16,17] that ordering in cubic III-V solid solutions can produce spontaneous polarization (or change it), an effect not unexpected also in the XN’s. Even in the random solution, short-range order in the

form of bond alternation may alter the local electronic structure, hence the polarization.

Devices: an example – Polarization fields offer new possibilities for device design, and concurrently may affect their performance. As a typical example, in Fig.1 we sketch a simple near-UV detector composed of a small- x , undoped $\text{In}_x\text{Ga}_{1-x}\text{N}$ active layer cladded by thick p - and n -doped GaN layers. As predicted by Eq. 6, in the active quantum well there is an internal field, which extracts the photogenerated carriers from the active region and lets them be easily collected by a small reverse bias. The efficiency of this device should be very high since essentially no tunneling is involved.

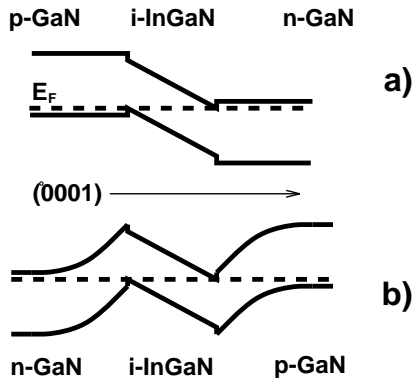


FIG.1 Electronic potential in the UV detector.

The key issue in this device is the crystallographic orientation and ensuing polarity of the epitaxially grown multilayer. Assuming for definiteness $x=0.1$, if the orientation is (0001) the correct sequence is p - i - n : the polarization-induced internal field (Eq.(6)) in the strained InGaN well points in the (000 $\bar{1}$) direction, and provides the desired performance (Fig. 1a). The reverse sequence n - i - p would be highly inefficient for this specific application (Fig. 1b). The existence of such effects of polarization fields, which may limit or enhance device performance, should be kept in mind in practical work.

Another potentially useful aspect is that the active layer thickness may be chosen so that the potential drop equals the difference of the Fermi levels of the n and p regions. The Fermi level is thus equalized across the system with flat bands conditions in the doped regions, i.e. no accumulation or depletion layers: assuming as above that $x=0.1$, the internal field is 20 mV/Å, so that to obtain a ~ 3 eV potential drop the layer should be ~ 150 Å thick. Further, to avoid strain effects, quaternary $\text{Al}_y\text{In}_w\text{Ga}_{1-w-y}\text{N}$ cladding layers could be used, with w and y tuned for lattice matching to $\text{In}_x\text{Ga}_{1-x}\text{N}$: the internal field in the QW will still be non-zero for any x , y , and w since in matching conditions $\text{Al}_y\text{In}_w\text{Ga}_{1-w-y}\text{N}$ has a larger spontaneous polarization than $\text{In}_x\text{Ga}_{1-x}\text{N}$.

In closing, we note that existing device realizations,

e.g. in the area of optical modulation in II-VI nanostructures [18], already exploit built-in piezoelectric polarization fields. There are, however, at least three major elements of novelty in the nitrides: first, spontaneous polarization, producing fields comparable to, or larger than the piezoelectric ones; second, the unusual magnitude of the fields, typically 2 orders of magnitude larger than in II-VI's; third, the giant band gap bowing [19] upon alloying (e.g. of GaN with GaAs), adding further degrees of freedom to nanostructure design.

In summary, we have discussed theory and applications of macroscopic polarization concepts to multilayers and devices made of III-V nitride compounds. We believe that these new concepts will contribute to open a very fruitful field for device design and simulation, and basic investigations of polarized semiconductors.

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